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The Content of Copper and Heavy Metals in the Multilayer Soil Mud from the Buchim Lake Under the Buchim Mine's Waste Dump, Republic North Macedonia

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The intense mineral extraction in mining areas during the last several decades has produced a large amount of waste material and tailings, which release toxic elements to the environment. The aim of the study was to determine in two vertical profiles/sections (1 and 2) the heavy metal contents of samples derived from six samples, three from each section located in the porphyry copper mine Buchim area, Republic North Macedonia. The results have been compared to new Dutchlist (DL) and Kabata-Pendias (KP) standards and the following was concluded: As values ranged 14.985÷60.131 mg kg^{-1} with 4 samples above the target value of the DL (29 mg kg^{-1} As) and 6 above standard values given in KP value (5 mg kg^{-1} As), in that context Co values ranged 11 ÷57 mg kg^{-1} with 6 values above the target value of the DL (9 mg kg^{-1} Co) and 5 above standard values given in KP value (12 mg kg^{-1} Co), Cr with range 29.32÷75.76 mg kg^{-1} with 6 over KP value (10 mg kg^{-1} Cr) and none above the target value of the DL (100 mg kg^{-1} Cr), Cu with range 2694÷6749 mg kg^{-1} with 6 samples above the target value of the DL (36 mg kg^{-1} Cu) and 6 above standard values given in KP value (20 mg kg^{-1} Cu), Ni with range 59.57÷105.98 mg kg^{-1} with 6 samples above the target value of the DL (35 mg kg^{-1} Ni) and 6 above standard values given in KP value (20 mg kg^{-1} Ni), Pb with range 27.06 ÷96.08 mg kg^{-1} with 1 sample above the target value of the DL (85 mg kg^{-1}Pb) and 6 above standard values given in KP value (25 mg kg^{-1}Pb), Zn with range 147÷273 mg kg^{-1} with 6 over target value of the DL (140 mg kg^{-1} Zn) and 6 above standard KP value (64 mg kg^{-1} Zn), V with range 34.44÷92.57 mg kg^{-1} with 5 over target value of the DL (42 mg kg^{-1} V) and one above KP value (90 mg kg^{-1} V).In order to compare the level of contamination, the contamination factor (C_f^i), degree of contamination (C_d), and pollution load index (PLI) were computed. Serious numbers were found for Cu, As, Zn, Co and Ni, which exceeded standard values at almost all samples from both vertical sections. Compared from section 1 and section 2, pollution load index increased by 13.43%, which in almost all samples was classified as heavily polluted to extremely polluted. The fact that mining activities at the Buchim Mine last for almost 40 years, the presence of heavy metals in soils at a serious level is understandable. The high level of contamination is a result of heavy metal persistence and non-biodegradability.

Key words: *soil, pollution, copper, porphyry, Buchim*

1. INTRODUCTION

A very serious environmental problem around the World poses toxicity and persistence of heavy metals which are accumulated in the environment as the result of diverse industrial activities. As it is already well known there are many different sources of heavy metal contaminants, including mining and metallurgical industries [1].

With the rapid development of mining activities landscape changes as well as environmental pollution have become still more serious. Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust [2],

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[3], [4], [5]. Copper mines with open ore pit type, where the intense mineral extraction has produced a large amount of waste material accumulated on the heaps or tailings [6], represent potentially emission source of heavy metals in the air, soil and water. Also, other pollution contributing processes are: minerals blasting, drilling and crushing, their loading and transportation to processing and flotation plants. Without proper management, mines and tailings are the source of heavy metals, which are washed out by precipitation and can contaminate all environmental components [7]. The extent and degree of heavy metal contamination vary depending upon the mineralogical and geochemical characteristics of both ore and host rocks [8]. We would like to stress out that soil is a critical environment because it is able to accumulate pollutants produced by anthropogenic activities, such as mining and processing of ore, industry, agriculture, traffic, etc. The transport of heavy metals in soil is the result of processes between soil and metal components, which include processes of physical, chemical, and biological nature [9]. However, soil is not only a passive acceptor of heavy metals, polluted soils become a source of contamination for other environmental components and the food chain [10]. In addition, heavy metals are non-degradable and persistent, their presence in soil is stable and long-term [12]. In the Republic North Macedonia, a lot of attention has been paid to the area of the Buchim Mine which is considered environmentally loaded and unhealthy. There, high levels of heavy metals were found not only in soil, water or sediment samples [11], [12], [13], [14], [15], but several studies detected extremely high levels of heavy metals in plants [16], [17]. The aim of the study was (1) to determine the level of contamination with heavy metals in the area of Buchim Lake just below the Buchim Mine waste dump in two vertical soil sections (1A-C, 2A-C), (2) to compare the level of contamination between the studied sections using the contamination factor, degree of contamination, and pollution load index, (3) to assess the correlation relationship between heavy metals and significant differences in heavy metal pollution between the studied sections.

2. MATERIALS AND METHODS

For almost 40 years mining activities in the region of the Buchim Mine were focused on copper and gold ore mining and processing. Moreover, based on the environmental regionalization, the area is considered environmentally loaded and hazardous for human health. Mining activities started here in the 1979 and peaked during the period 2005-2017. During the years, production mine areas, heaps of waste material and tailing ponds significantly increased their volumes and became the source of undesirable substances, heavy metals. From the geographical point of view, the area (ca.375 km^2) is situated in the Radovis Valley and Damjan's Field. The population (ca.16000) is concentrated predominantly in the city of Radovis and adjacent villages. Climatologically the region is characterized as moderate Adriatic-continental climate with coldest month January with 1.2^{o}C as an average and warmest months July and August with an average tempe ratures of 23^{o}C. Position of the sampling sites is shown in Figure 1 and Figure 2.

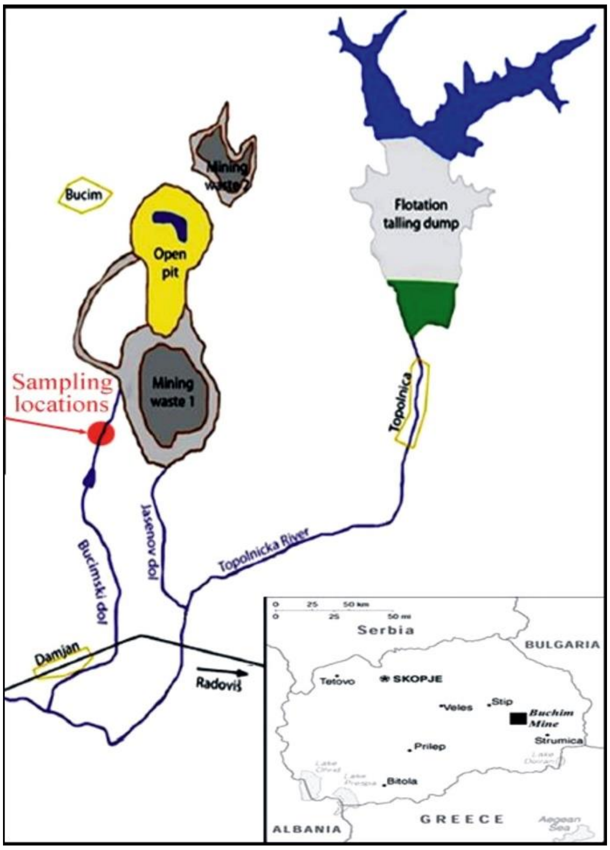

Figure 1 - Position of the Buchim Mine, its facilities and sampling location

The tailing pond, copper processing plant, and a couple heaps of waste material randomly distributed over the study area represent the main sources of toxic elements (Figure 1). The tailing pond is localized in the western part of the Radovis city cadastre in the immediate vicinity of the Topolnica village. Waste material occurring in the upper part of the pond is of powder consistency. The plant located in the Buchim Mine has long been used for copper ore processing. Mud soil sampling from 2 sampling sites in the active mining area of the Buchim Mine was carried out (Fig. 2) from the horizons A, B and C (5, 15, 20/25 cm), which are usually under water while during summer/-autumn season are dry. From each sampling site three samples were collected. Samples were stored in plastic bags, air dried in laboratory conditions, crushed, sieved through 2 mm sieve and grinded in agate mill to obtain particles below 0.1 mm. Then, the samples were digested by applying a mixture of HNO_3, $HClO_4$, HF and HCl in accordance with the international standards ISO 14869-1:2001. The obtained solution is filtered through filter paper and quantitatively transferred into a 25 ml volumetric flask. The flask is supplemented with distilled water. Analysis of the soil samples has determined the content of a total of 20 elements (As, Al, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) with application of the atomic emission spectrometer with inductively coupled plasma (ICP-AES), model Varian 715-ES. Both soil certified reference material (JSAC 0401) and spiked intra-laboratory samples were analyzed at a combined frequency of 20% of the samples. Recovery for spiked samples ranged 90-110%, while the recovery for the certified reference material ranges 94-108%.

a)

b)

c)

d)

Figure 2 - Bucim Lake and positions of the soil vertical sections sampling locations a) Buchim Lake and the first sampling position; b) The second sampling position; c) The process of sampling at the second position; d) a variety of colored vertical layers at the second sampling position

3. RESULTS AND DISCUSSION

As we assumed, mining and ore processing in the active Buchim Mine during the period of almost 40 years have left its certain environmental footprint. The latest study and laboratory results of 20 elements (As, Al, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn), confirmed their increased contents, sometimes even of several magnitudes higher than allowed or standard values, especially for the heavy metals such are As, Co, Cr, Cu, Ni, Pb, V and Zn (Table 1).

Since we were exactly interested on heavy metals pollution, ours further efforts were diverted in direction of analyzing and discussing heavy metals and their statistical "behavior" in the sampled soil horizons around the Buchim Mine. The most intriguing results have been found, in regards to the new Dutchlist [18] and other standard values [19], for arsenic, cobalt, chromium, copper, nickel, lead, zinc and vanadium. Namely, arsenic showed values in the range 14.985÷60.131 mg kg-1 As averaging 36.41 mg kg-1 As, which pointed to values up to 2÷12 times higher than standard values. Cobalt values were in the range 11÷57 mg kg-1 Co, averaging 33.70 mg kg-1 Co, which pointed to values up to 1.5÷5 times higher than standard values. Chromium showed values within range 29.32÷75.76 mg kg-1 Cr, averaging 61.75 mg kg-1 Cr, which according to [20] were not above the standard values while according to [21] were 3÷7 times higher than standard values.

Copper values were within the range 2694÷6749 mg kg^{-1} Cu, averaging 4189.92 mg kg^{-1} Cu that is 74÷337 times higher than respective standard values. Nickel values within range 59.57÷105.98 mg kg^{-1} Ni, averaging 78.89 mg kg^{-1} Ni showed nickel presence in general is 2÷5 times higher than respective standard values.

Table 1. Analysis results of soil mud samples from the vicinity of the Buchim Mine (Buchim Lake), Republic North Macedonia (all the results are in mg kg^{-1})

Elem.	1A	1B	1C	2A	2B	2C	Min.	Max.	Averag	Std.dev.
Al	29502.52	67419.23	35724.11	19327.10	58138.51	46242.57	19327.10	67419.23	42725.67	18061.36
As	14.99	35.31	34.25	21.94	51.86	60.13	14.99	60.13	36.41	17.18
B	14.73	15.97	9.18	10.98	15.58	17.05	9.18	17.05	13.92	3.12
Ba	76.38	52.44	57.48	35.67	49.54	125.86	35.67	125.86	66.23	32.05
Ca	1002.25	665.25	1695.59	1259.98	591.64	639.48	591.64	1695.59	975.70	437.42
Co	34.75	11.00	30.96	57.00	24.07	44.43	11.00	57.00	33.70	15.97
Cr	74.57	61.73	60.62	29.32	68.47	75.76	29.32	75.76	61.75	17.08
Cu	2694.28	5833.58	3816.52	2777.73	3268.13	6749.27	2694.28	6749.27	4189.92	1701.31
Fe	33167.42	30907.67	28019.67	14095.58	32116.00	45223.00	14095.58	45223.00	30588.22	10018.68
K	7930.27	17319.44	10920.52	2237.11	12159.21	10792.86	2237.11	17319.44	10226.57	4978.97
Li	9.53	9.66	8.20	4.47	10.50	14.14	4.47	14.14	9.42	3.15
Mg	1384.00	418.07	638.90	2344.96	1461.50	2138.69	418.07	2344.96	1397.69	772.80
Mn	1739.22	628.10	615.34	4698.37	760.58	1428.26	615.34	4698.37	1644.98	1565.59
Na	608.03	2857.57	7070.13	220.45	997.93	455.02	220.45	7070.13	2034.86	2643.10
Ni	59.57	61.76	105.98	83.37	67.43	95.24	59.57	105.98	78.89	19.07
P	596.17	826.19	799.70	474.72	827.82	874.63	474.72	874.63	733.20	159.76
Pb	71.68	83.55	37.15	27.06	45.78	96.08	27.06	96.08	60.22	27.58
Sr	15.51	198.44	25.28	10.99	16.41	14.42	10.99	198.44	46.84	74.42
V	88.29	67.08	75.19	34.44	81.25	92.57	34.44	92.57	73.14	21.03
Zn	147.48	132.15	235.57	272.53	172.35	249.94	132.15	272.53	201.67	58.53

Lead values were within the range 27.06÷96.08 mg kg^{-1} Pb, averaging 60.22 mg kg^{-1} Pb that is 1.5÷4 times higher than respective standard values. Zinc values were within the range 147÷273 mg kg^{-1} Zn, averaging 201.67 mg kg^{-1} Zn, which is 1.5÷4 times higher than respective standard values. Vanadium values were within the range 34.44÷92.57 mg kg^{-1} V, averaging 73.14 mg kg^{-1} V which is 1.5÷3 times higher than respective standard values. For better spatial insight into those findings we plotted measured concentrations of certain heavy metals versus respective standard values, both, [18] and [19] (Fiure 3).

Bivariate statistics has been applied in order to determine the correlation degree between the examined elements, which shows that when the absolute value of the correlation coefficient extends from 0.3 to 0.7, then, it is a matter of good association of the elements, and when such values extend from 0.7 to 1.0, then we can say that there is strong connection between the examined elements. Significant correlation factors, were determined for the mineral pairs Co-Zn (0.830), Cr-Pb (0.702), Cr-V (0.988), Cu-Pb (0.775) and Ni-Zn (0.824). All of them reflect natural affinity of aforementioned elements to enter into solid solution with each other.

For determination of metal pollution in soils, contamination factor (C_f^i) and degree of contamination (C_d) were used [20], Table 2. The C_f^i is a singlemetal index determined by the relation:

$$C_f^i = \frac{C_{0-1}^i}{C_n^i}$$

where: C_{0-1}^i– concentration of metal in the sample

C_n^i– background level of metal in upper Earth's crust

The background values of metals (C_n^i) in natural soils were considered as 29, 9, 100, 36, 35, 85, 42 and140 mg/kg for As, Co, Cr, Cu, Ni, Pb, V and Zn, respectively [18] as well as compared to those of 5, 12, 10, 20, 20, 25, 90 and 64 mg/kg for As, Co, Cr, Cu, Ni, Pb, V and Zn, respectively [19]. Here in our study we used four classes that were recognized by [20]:

Class	Factor of contamination	C_f^i	C_d
(i)	low	< 1	< 8
(ii)	moderate	1 - 3	8 - 16
(iii)	considerable	3 - 6	16 - 32
(iv)	very high	≥ 6	≥ 32

The C_d is a measure of the degree of overall contamination in a particular sampling site and was defined as the sum of all C_f^i:

$$C_d = \sum_{i=0}^{n} C_f^i$$

The C_d, according to [24], was divided into four groups see above.

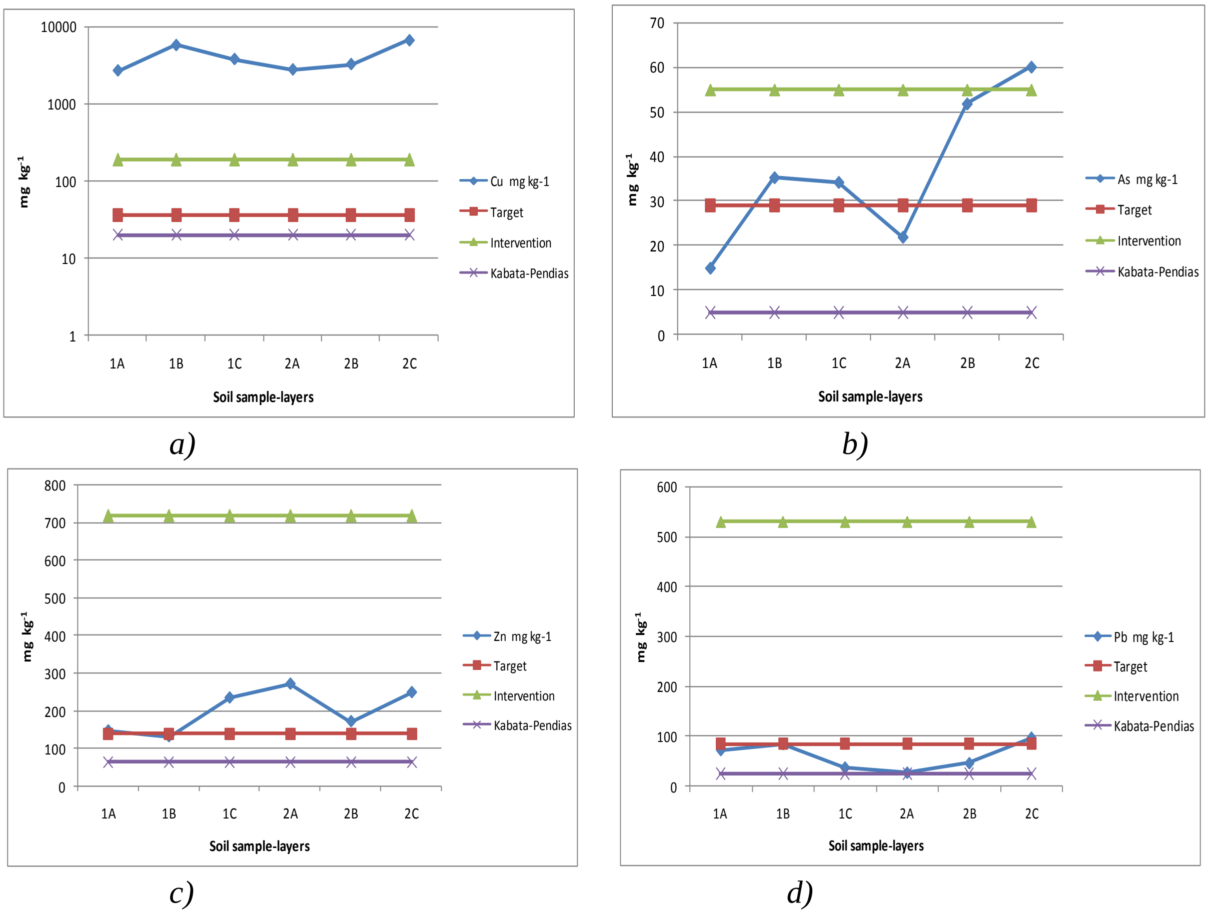

Figure 3 - Concentrations of Cu (a), As (b), Zn (c) and Pb (d) in comparison with relevant reference values

Pollution load index (PLI) proposed by [20], [21] is an empirical index that comparatively assesses the level of heavy metal pollution for each sampling site. PLI was calculated by the relation:

$$PLI=(C_{f1} x\ C_{f2} x C_{f3} x \ldots . x C_{fn})^{1/n}$$

where: n – number of assessed metals (n = 8 herein)

Cf – contamination factor of individual pollutant

The value of PLI was classified into four groups [11]:

group	pollution	PLI
(i)	no	< 1
(ii)	moderate	1 - 2
(iii)	heavy	2 - 3
(iv)	extreme	≥ 3

As can be seen from Table 2 above, pollution load index (PLI), ranged from 1.840 to 3.394, suggesting moderate to extreme pollution according to previously mentioned classification [11], although the majority of PLI values were in the heavy pollution class.

Mining and smelting activities in the study area were focused predominantly on copper production, therefore contamination with this metal has for long term been considered the most serious [12], [13], [14], [15], [16].

The concentrations of copper and the other 7 heavy metals are highest in layers C (footwall) because the concentration of those metals while in solution was highest because the largest were the extracts from the primarily deposited mineralized rocks (waste dump) in the Buchim mine in which vicinity is located Buchim Lake (Figure 1).

Table 2. Values of contamination factor (C_f) and degree of contamination (C_d) for each sampled level in both evaluated sections/profiles (1 and 2) as well as pollution load index (PLI)

Sampl.	Contamination factor (C_f)								C_d (degre of contamination)	PLI
	As	Co	Cr	Cu	Ni	Pb	V	Zn		
1A	0.517	3.861	0.746	74.841	1.702	0.843	2.102	1.053	85.665	*2.083*
1B	1.217	1.222	0.617	162.044	1.765	0.983	1.597	0.944	170.389	*2.107*
1C	1.181	3.440	0.606	106.014	3.028	0.437	1.790	1.683	118.179	*2.383*
1 aver.	*0.972*	*2.841*	*0.656*	*114.300*	*2.165*	*0.754*	*1.830*	*1.227*	*124.745*	*2.291*
2A	0.756	6.333	0.293	77.159	2.382	0.318	0.820	1.947	90.009	*1.840*
2B	1.788	2.674	0.685	90.781	1.927	0.539	1.935	1.231	101.560	*2.282*
2C	2.073	4.937	0.758	187.480	2.721	1.130	2.204	1.785	203.088	*3.394*
2 aver.	*1.539*	*4.648*	*0.579*	*118.473*	*2.343*	*0.662*	*1.653*	*1.654*	*131.552*	*2.599*

The results of the waters (source Bucim Mine laboratory) in those first leached solutions reached up to 480 mg l^{-1} Cu, while much later when the material was repeatedly leached the copper content dropped to 100 mg l^{-1} Cu in the water solutions. This indicates that the precipitation of heavy metals and their deposition in mud soil is directly proportional to the amount of dissolved metals in the water over a period of time. This is confirmed by the fact that our experiment, where in layers A of mud soil samples which are the most recently exposed, copper content and other treated heavy metals, is significantly lower. These findings are quite in line with findings of some other researchers for similar worldwide localities [22], [23], [24].

4. CONCLUSION

The imediate area of the Buchim lake around active Buchim Mine, showed increased concentrations of As (14.985÷60.131 mg kg-1), Cu (2694÷6749 mg kg-1), Pb (27.06 ÷96.08 mg kg-1) and Zn (147÷273 mg kg-1) in analyzed soil mud from the botom of the lake. Computed contamination factor (C_f^i) indicated low to very high values (especially for Cu), degree of contamination (Cd) showed very high degree of contamination while the pollution load index (PLI) indicated heavy to extreme pollution.

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REZIME

SADRŽAJ BAKRA I PRATEĆIH ELEMENATA I VIŠESLOJNOM BLATNJAVOM ZEMLJIŠTU IZ BUČIMSKOG JEZERA ISPOD JALOVIŠTA RUDNIKA „BUČIM“, REPUBLIKA SEVERNA MAKEDONIJA

Intenzivna eksploatacija minerala u rudarskim područjima tokom poslednjih nekoliko decenija producirala je i velike količine otpadnog materijala i jalovine, koji oslobađaju toksične elemente i životnu sredinu. Cilj ovoj proučavanja je bio da se u dva vertikalna profila/preseka (1 i 2) utvrde sadržaji teških metala u uzorcima dobijenih iz šest uzorarka, po tri iz svakog profila koji se nalaze na području rudnika porfirskog bakra Bučim, Republika Severna Makedonija. Rezultati su upoređeni sa standardima nove holandske liste (DL) i standardima Kabata-Pendias (KP) i zaključeno je sledeće: vrednosti As su se bile u opsegu 14,985÷60,131 mg kg^{-1} sa 4 uzorka iznad ciljne vrednosti date u DL (29 mg kg^{-1} As) i 6 iznad standardnih vrednosti datih u KP (5 mg kg^{-1} As), u tom kontekstu vrednosti Co su bile u opsegu 11 ÷57 mg kg^{-1} sa 6 vrednosti iznad ciljne vrednosti date u DL (9 mg kg^{-1} Co) i 5 iznad standardnih vrednosti datih u KP (12 mg kg^{-1} Co), Cr u opsegu 29,32÷75,76 mg kg^{-1} sa 6 vrednosti iznad KP vrednosti (10 mg kg^{-1} Cr) i nijedne iznad ciljne vrednosti u DL (100 mg kg^{-1} Cr), Cu sa opsegom 2694÷6749 mg kg^{-1} i sa 6 uzoraka iznad ciljne vrednosti u DL (36 mg kg^{-1} Cu) i 6 iznad standardne vrednosti u KP (20 mg kg^{-1} Cu), Ni sa opsegom 59,57÷105,98 mg kg^{-1} sa 6 uzoraka iznad ciljnje vrednosti u DL (35 mg kg^{-1} Ni) i 6 iznad standardnih vrednosti u datih u KP (20 mg kg^{-1} Ni), Pb sa opsegom 27,06 ÷96,08 mg kg^{-1} i 1 uzorkom iznad ciljne vrednosti u DL (85 mg kg^{-1}Pb) i 6 iznad standardnih vrednosti datim u KP (25 mg kg^{-1}Pb), Zn sa opsegom 147÷273 mg kg^{-1} sa 6 vrednostima iznad ciljne vrednosti date u DL (140 mg kg^{-1} Zn) i 6 iznad standardne KP vrednosti (64 mg kg^{-1} Zn), V sa opsegom 34,44÷92,57 mg kg^{-1} i 5 vrednosti iznad ciljne vrednosti u DL (42 mg kg^{-1} V) i jedne iznad KP vrednosti (90 mg kg^{-1} V). Da bi se uporedio nivo kontaminacije, izračunati su faktor kontaminacije (C_f^i), stepen kontaminacije (C_d), i indeks zagađenja (PLI). Ozbiljne vrednosti su pronađene za Cu, As, Zn, Co i Ni, koje su prevazišle standardne vrednosti skoro u svim uzorcima iz oba vertikalna profila/preseka. U poređenju profil 1 sa profilom 2, indeks zagađenja je povećan za 13,43%, što je skoro u svim uzorcima klasifikovano kao visoko zagađeno do izuzetno zagađeno. Činjenica je da rudarske aktivnosti rudnika Bučim traju gotovo 40 godina, pa je razumljivo prisustvo teških metala u ozbiljnim nivoima. Visok nivo kontaminacije rezultat je istrajnosti teških metala i bio-nerazgradljivosti.

Ključne reči: *zemljište, zagađenje, bakar, porfirski, Bučim*